

**Argonne National Laboratory**

**FABRICATION AND EVALUATION OF  
THORIA-URANIA FUEL MATERIAL**

**by**

**E. D. Lynch and J. H. Handwerk**

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## FABRICATION AND EVALUATION OF THORIA-URANIA FUEL MATERIAL

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### ABSTRACT

Various fabrication techniques for  $\text{ThO}_2\text{-UO}_2$  compositions such as dry-pressing, hot-pressing, and slip-casting were studied. A procedure was established for large-scale fabrication of a  $\text{ThO}_2\text{-U}_3\text{O}_8$  composition to be used in a fuel loading. The effects of variables in fabrication and materials on the sintering behavior of  $\text{ThO}_2\text{-U}_3\text{O}_8$  compositions were evaluated.

Various samples were prepared for the evaluation of the behavior of  $\text{ThO}_2\text{-UO}_2$  compositions under irradiation. In addition to the irradiation specimens for material evaluation, samples differing in porosity were prepared for a study of the effect of voids on irradiation behavior, and other samples were prepared for use in determining the effects of dispersed metal fibers on the irradiation behavior of  $\text{ThO}_2\text{-UO}_2$  fuels.

### INTRODUCTION

The development of ceramic oxide fuel materials at Argonne National Laboratory was initiated because of their potential application to the boiling-water-reactor program. Fuels for this type of reactor system must be highly resistant to water corrosion at elevated temperatures and must be dimensionally stable to burnup of fissionable atoms. Ceramic oxide-type fuels have a great potential for satisfying these two basic requirements of the boiling-water-reactor fuel.

The thoria-urania system was selected for study since it appeared to have some nuclear and economic advantages over other oxide systems. These advantages result primarily from the use of thorium oxide as a major portion of the fuel composition.

Thorium dioxide is the only solid oxide phase of thorium, and this oxide has excellent temperature stability, has no harmful phase transformations, and is very resistant to corrosion by water. As a result

of these characteristics of thorium, compositions in the system  $\text{ThO}_2\text{-UO}_2$  are more resistant to oxidation, more resistant to water corrosion, and more stable at high temperatures than uranium dioxide.

The construction of a thermal breeder reactor or prolonged reactivity of a fuel-core loading is a possibility through the use of thorium atoms in the fuel. Natural thorium ( $\text{Th}^{232}$ ) will absorb thermal neutrons to form  $\text{Th}^{233}$  which, through  $\beta$  decay, forms  $\text{U}^{233}$ , and this isotope will fission with thermal neutrons.

Although the use of thorium in a nuclear reactor has many advantages, some factors may limit the use to some extent. Thorium breeder reactors require large volumes for efficient breeding, since thorium absorbs thermal neutrons to a limited extent. This, in turn, requires reprocessing of large volumes of material during the extraction of  $\text{U}^{233}$ .

The neutron absorption in thorium under practical reactor conditions is accompanied by the formation of  $\gamma$  radioactive by-products. In addition to the  $\gamma$  activity,  $\text{U}^{233}$  is very toxic because of its relatively short half-life and  $\alpha$  radioactivity. As a result,  $\text{U}^{233}$  will require remote or shielded facilities for handling.

These disadvantages should not seriously impede the use of thorium as a fertile material, and, as nuclear technology progresses, thorium-based ceramics should become an important material for nuclear-reactor fuels.

#### SOLID SOLUTION IN THE SYSTEM $\text{ThO}_2\text{-UO}_2$

The formation of a complete series of solid solutions between thorium dioxide and uranium dioxide was reported by Lambertson *et al.*,<sup>1</sup> as shown in Fig. 1. When heated in hydrogen or in vacuum, this system exhibits complete miscibility to the liquidus. The solid solutions formed had the fluorite structure, and the lattice parameters followed Vegard's law quite closely.

The addition of  $\text{ThO}_2$  to  $\text{UO}_2$  helps to stabilize the structure against oxidation. Oxidation does occur on heating in air and results in a limited range of solid solutions in the hyperstoichiometric system. Hund and Niessen<sup>2</sup> reported that solid solutions containing up to 56.5 m/o  $\text{UO}_2$  were stable to oxidation; Anderson *et al.*<sup>3</sup> reported that the fluorite structure was retained in an oxidizing atmosphere for solid solutions containing up to 78 m/o  $\text{UO}_2$ . The differences may be accounted for by the different methods used in preparation of the solid solutions.



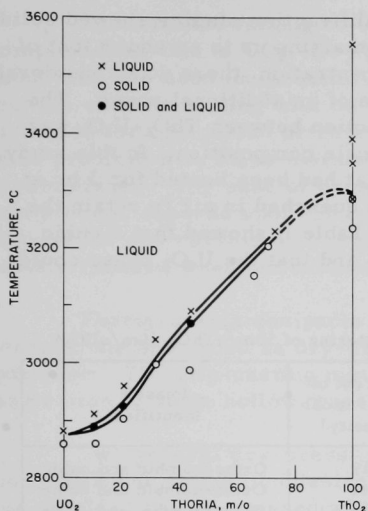


Fig. 1. ThO<sub>2</sub>-UO<sub>2</sub> Phase-equilibrium Diagram

Thoria-urania solid solutions are conveniently formed by codigestion<sup>2</sup> or coprecipitation<sup>3,4</sup> techniques. In the codigestion technique, soluble salts of thorium and uranium, preferably nitrates, are dissolved in water, evaporated to dryness, and calcined to decompose the materials to oxides. In the precipitation technique, solutions of thorium and uranium salts are introduced into excess ammonia solution, and the solid solution of these salts is precipitated. Calcination in air is used to convert the product to oxide. In either case, solid solutions of the oxides of thorium and uranium may be produced by calcination in air.

The advantage of either of these processes lies in the intimacy of mixing achieved through the use of solutions. The materials formed by coprecipitation more nearly approach the equilibrium phase for the composition being prepared,

since there is a tendency for the nitrates to crystallize independently in codigestion, due to solubility differences. However, when the end products are sintered at high temperature, there is no apparent difference in the solid solution. The solid solutions formed by these processes are hyperstoichiometric and require sintering in a reducing atmosphere such as hydrogen to achieve stoichiometry.

Solid solutions may also be formed by direct reaction of any of the oxides of uranium and ThO<sub>2</sub> at elevated temperatures. In the case of UO<sub>2</sub>, a protective atmosphere is required to achieve direct reaction or to obtain densification, since there is approximately a 30 v/o increase resulting from the conversion of cubic UO<sub>2</sub> to orthorhombic U<sub>3</sub>O<sub>8</sub> when UO<sub>2</sub> is heated in the presence of oxygen.

The reports of Warde and Johnson<sup>5</sup> and Hoekstra *et al.*<sup>6</sup> showed U<sub>3</sub>O<sub>8</sub> to be a stable phase in an oxidizing atmosphere to about 1150°C, and, at higher temperatures, U<sub>3</sub>O<sub>8</sub> decomposes to lower oxide phases. The lack of any sudden volume changes during this decomposition indicated a possibility for forming dense solid-solution compacts by reaction of ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> in an oxidizing atmosphere.

The formation of solid solutions from the reaction of ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> in air was reported by Handwerk *et al.*<sup>7</sup> Compositions containing up to 80 w/o UO<sub>2</sub>, added as U<sub>3</sub>O<sub>8</sub>, were successfully sintered to high densities in air at

temperatures of 1700°C and above. X-ray diffraction studies showed solid solutions were formed for compositions containing up to an equivalent of 60 w/o  $\text{UO}_2$ . For higher levels of  $\text{UO}_2$  concentration, there was considerable broadening of diffraction lines and evidence of an additional phase. The effect of temperature on solid-solution reaction between  $\text{ThO}_2$ - $\text{U}_3\text{O}_8$  was reported by Handwerk and Hoenig<sup>8</sup> for a single composition. In this study, X-ray examination was made of samples that had been heated for 3 hr at temperatures between 1000 and 1500°C and quenched in air to retain the high-temperature structure. The results (Table I) showed that a cubic solid-solution phase was present at 1000°C and that the  $\text{U}_3\text{O}_8$  phase could no longer be detected at 1300°C and above.

TABLE I. Development of Properties during Sintering of 30m/o $\text{ThO}_2$ -70m/o $\text{UO}_2$ \*

Draw-trial** Temperature, °C	Diametrical Shrinkage, %	Bulk Density, g/cc	Percent of Theoretical Density†	Phases Identified
1000	0	4.2	39	Orthorhombic and cubic
1100	0.5	4.7	44	Orthorhombic and cubic
1200	4.5	5.9	56	Orthorhombic and cubic
1300	10.7	8.5	80	Cubic
1400	12.2	9.7	92	Cubic
1500	12.9	9.8	92	Cubic

\* $\text{UO}_2$  added as equivalent  $\text{U}_3\text{O}_8$  for air sintering.

\*\*"Draw trial"--see page 14 for explanation.

†Based on theoretical density of 10.67 for  $\text{Th}_{0.3}\text{U}_{0.7}\text{O}_{2.0}$ .

The solid solutions formed by the reaction of  $\text{ThO}_2$  and  $\text{U}_3\text{O}_8$  in air are hyperstoichiometric. Studies of the stability and X-ray parameter relationships in this system have been reported by Lynch *et al.*<sup>9</sup> and are the subject of a later report from this Laboratory.<sup>10</sup>

## FABRICATION OF THORIA-URANIA SOLID-SOLUTION COMPACTS

The preparation of thoria-urania materials for fabrication into usable shapes varies somewhat with the method selected for formation of the solid solution.

When the direct reaction of  $\text{ThO}_2$ - $\text{UO}_2$  in an inert or reducing atmosphere is used, very intimate mixing of the oxides is necessary to produce a homogeneous solid solution. Dry grinding of the oxides in ball mills has been used, but the prolonged grinding required for proper distribution may result in contamination. Uranium dioxide is more easily blended with thoria by ball-milling with sufficient water to form a thin slurry of the mixture. Such a slurry will be well-mixed after milling 3-4 hr and may be dewatered and the cake granulated to form a powder suitable for fabrication.

The intimate mixing of  $U_3O_8$  with  $ThO_2$  appears to be easier to accomplish than that of  $UO_2$ . Dry grinding of these materials for periods of about 3 hr has been found sufficient to break up agglomerates of  $U_3O_8$  and provide uniform mixing with the  $ThO_2$ . A dry-milling procedure may be also used for codigested or coprecipitated materials. Intimacy of mixing is no problem with these materials since this intimacy has already been accomplished. The ease of preparation of these materials for a fabrication process depends upon the temperature at which the decomposition calcination was carried out. Particle size of the calcined material is more readily reduced when the calcination temperature is below  $1000^\circ C$ .

Thoria-urania compacts may be fabricated by any of the common ceramic methods such as dry-pressing, hot-pressing, slip-casting, or extrusion. The slip-casting method has been used primarily only for the fabrication of some hollow-ware shapes.

Two general dry-pressing procedures have been used, depending on the quantity of production desired. For producing a small number of pieces, fine powders can be pressed without additions, in steel dies, at pressures of 703 to  $1406 \text{ kg/cm}^2$ . For ease in handling, the dry strength can be improved by adding 1 to 3 w/o of an organic binder such as polyethylene glycol. Binders are most satisfactorily added by blending a solution of the binder with the dry powder. Isostatic pressing, with or without binders, has also been used to improve the density of compacts prior to sintering.

Fabrication of large quantities of shapes requires a free-flowing material for use in automatic presses. A free-flowing material may be prepared by a granulation procedure. An effective addition for producing a granulated material is polyvinyl alcohol. The powdered materials are blended with from 1 to 3 w/o polyvinyl alcohol and approximately 12 w/o water, and the dampened material is forced through a 16-mesh screen to form granules. Reduction of the water content by drying at  $80^\circ C$  yields free-flowing granules that are readily broken down by the application of pressure in the die. Automatic pressing normally requires some die lubrication, and the lubricant commonly is added to the granulated material.

Thoria-urania materials have been hot-pressed by simultaneous application of heat and pressure in graphite molds. Samples have been prepared without evidence of carbide formation, at mold temperatures of 1400 to  $1800^\circ C$ .

Mixtures of  $ThO_2-UO_2$  and  $ThO_2-U_3O_8$  have been slip-cast by procedures similar to that used for  $UO_2$ . Mixtures of  $UO_2$  and  $ThO_2$  were ground with water as the dispersion medium in steel ball mills with steel balls for a 72-hr period. The slurry was leached with  $HCl$  to remove iron contamination, and the settled powder was washed with water. A slip suitable for casting in plaster molds was formed by adjusting the pH of

the suspension to the range of 2 to 4. When  $U_3O_8$ - $ThO_2$  mixtures were used, it was found more satisfactory to mill the thorium separately and acid-leach to remove contamination. The pH of the thorium suspension was adjusted to about 6, and  $U_3O_8$  was added by ball-milling in a porcelain mill to form a suitable casting slip.

Thoria-urania shapes may be sintered in hydrogen, inert gas, vacuum, or air, depending on whether  $UO_2$  or  $U_3O_8$  is used as the source of uranium. Only  $ThO_2$ - $U_3O_8$  mixtures may be sintered in air. Compacts may be sintered to densities in excess of 90% theoretical at a temperature as low as  $1400^\circ C$ , but solid solution is more rapidly accomplished and higher densities attained in the range of  $1600$  to  $1750^\circ C$ . Intimacy of mixing is a controlling factor in both the time and temperature required to form a homogeneous solid solution. Sintering in vacuum has limitations in that the loss of uranium oxide from the material is appreciable in the temperature range required for solid-solution formation. When organic binders are used in fabrication, the sintering cycle is adjusted so that the heating rate is slow up to  $600^\circ C$  to enable the binders to be burned out without rupturing the compact.

A large-scale fabrication of  $ThO_2$ - $U_3O_8$  fuel was carried out at Argonne National Laboratory in the production of fuel for the BORAX-IV reactor.<sup>11</sup> The fuel loading and blanket assembly for this reactor required 166,000 pellets of thorium-urania 0.64 cm OD x 1.27 cm long and 23,000 pellets of  $ThO_2$  of the same diameter. A flow sheet of the fabrication procedure used for the fuel loading is shown in Fig. 2.

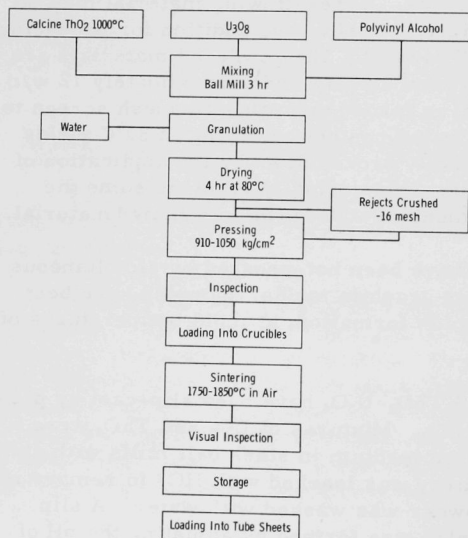


Fig. 2  
Flow Sheet for the Manufacture of  
Ceramic Fuel for BORAX-V Reactor



The fuel was prepared by air-sintering a  $\text{ThO}_2\text{-U}_3\text{O}_8$  mixture that contained 6.59 w/o highly enriched  $\text{U}_3\text{O}_8$ . It was found necessary to calcine the  $\text{ThO}_2$  to  $1000^\circ\text{C}$  to remove the approximately 0.7% volatile contaminants found in this material. Batch preparation was on the basis of 200 g of  $\text{U}_3\text{O}_8$ . This amount of  $\text{U}_3\text{O}_8$ , plus the required amount of  $\text{ThO}_2$  and a 2.5 w/o addition of polyvinyl alcohol, were mixed together for 3 hr in a 1-gal porcelain ball mill containing approximately 1 kg of balls. The mixed powder was moistened by an addition of 12 w/o of water containing 0.5% of aerosol. The dampened material was granulated through a 16-mesh screen, and the granules were dried at  $80^\circ\text{C}$  for 4 hr. Before pressing, 1 w/o of a mixture of 50% kerosene and 50% oleic acid were added to the granulated material as a die lubricant. Pellets were produced by pressing at 914 and  $1055\text{ kg/cm}^2$  in a double-acting press. After pressing, the pellets were heated overnight at  $260^\circ\text{C}$  to remove binders and were then sintered in a natural-gas-fueled furnace to a temperature of  $1700\text{-}1750^\circ\text{C}$  over a period of approximately 16 hr, including 2 hr at the peak temperature.

This procedure was very satisfactory, and the rejects were less than 4%. Pellet diameters were held in the range of  $0.581 \pm 0.005\text{ cm}$ , and the average apparent density was about 97% theoretical for the composition based on  $\text{ThO}_2\text{-UO}_2$ .

## MATERIALS EVALUATION

Sintering Behavior

The sintering behavior of urania-thoria compacts is influenced by several factors, such as starting-materials compositions, particle size, forming pressure, sintering atmosphere, and sintering temperature. The primary aims of the sintering operation for these materials are the formation of a homogeneous solid solution and the attainment of a high-density compact.

The effects of the fabrication parameters on sintering were studied for compositions across the  $\text{ThO}_2$ - $\text{UO}_2$  system. The materials used in this study were  $\text{ThO}_2$  and  $\text{U}_3\text{O}_8$ , the  $\text{U}_3\text{O}_8$  being added in an amount equivalent to the  $\text{UO}_2$  content desired. For this study,  $\text{U}_3\text{O}_8$  was prepared by heating minus 325-mesh  $\text{UO}_2$  in air to  $1000^\circ\text{C}$  for 2 hr and cooling slowly to room temperature. Conversion of the oxide was confirmed by X-ray analysis. The  $\text{ThO}_2$  was also calcined to  $1000^\circ\text{C}$ , and both oxides were passed through a 100-mesh screen to break up agglomerates.

The materials were prepared for fabrication and sintering as follows: A 1-w/o addition of polyethylene glycol was made to each thoria-urania composition as a binder. The compositions were wet-milled for 2 hr, and the water was removed by drying. Each composition was then mixed with a 2-w/o water addition to prepare them for pressing. Samples were fabricated by cold-pressing into cylinders approximately 1.9 cm diam by 1.27 cm long. Sintering was carried out in an oxidizing atmosphere by means of a natural-gas-fired furnace.

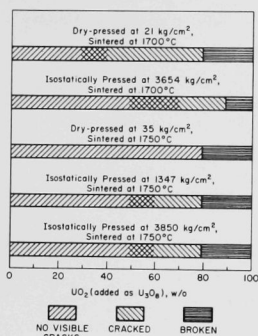


Fig. 3

The Effects of Composition and Fabrication Parameters on the Sintering of  $\text{ThO}_2$ - $\text{UO}_2$  Compacts

Sintered samples of these materials containing up to 25 w/o  $\text{UO}_2$  were reheated in air to  $1750$ - $1850^\circ\text{C}$  with no visible cracking and with negligible weight loss.

The effects of forming technique and sintering temperature on the fabricated appearance of these materials are shown in Fig. 3. Cracking appeared in samples containing more than 30 to 50 w/o  $\text{UO}_2$  (added as  $\text{U}_3\text{O}_8$ ) for materials sintered at  $1700^\circ\text{C}$ . When the sintering temperature was increased to  $1750^\circ\text{C}$ , samples containing greater than 50 w/o  $\text{UO}_2$  showed cracking.

The apparent densities\* of similarly processed materials sintered at  $1750^\circ\text{C}$  were determined; the results are shown in Fig. 4. The sintered densities increased with increasing forming pressure, but progressively decreased as the  $\text{UO}_2$  content of the mixture increased. Sintered samples of these materials containing up to 25 w/o  $\text{UO}_2$  were reheated in air to  $1750$ - $1850^\circ\text{C}$  with no visible cracking and with negligible weight loss.

\* Apparent density = weight/(bulk volume - volume of open porosity).

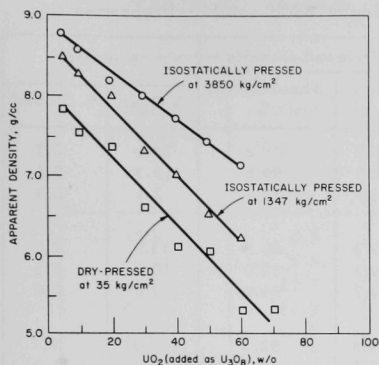


Fig. 4. Densities Attained for  $\text{ThO}_2\text{-UO}_2$  Compositions Sintered in Air at  $1750^\circ\text{C}$

$\text{UO}_2$  and greater. The use of additives with the materials of lower  $\text{UO}_2$  content was effective, and densities greater than  $9.0 \text{ g/cc}$  were readily obtained. Additions to the materials of higher  $\text{UO}_2$  content were not effective in densification, although  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  were effective in reducing the cracking of samples.

The effect of material preparation on the sintering behavior was investigated for some compositions containing greater than 30 w/o  $\text{UO}_2$ . Pellets approximately 1.90 cm diam by 2.54 cm long were made from  $\text{U}_3\text{O}_8\text{-ThO}_2$  mixtures and from materials prepared from the nitrates of urania and thoria. The  $\text{U}_3\text{O}_8\text{-ThO}_2$  mixtures were prepared by wet-milling for 72 hr, calcining at  $600^\circ\text{C}$ , preforming without binder at  $422 \text{ kg/cm}^2$ , and isostatically pressing at  $2812 \text{ kg/cm}^2$  prior to sintering. The codigested solid solutions were formed by evaporating to dryness a solution of uranyl nitrate and thorium nitrate. The nitrate solid solutions were calcined for 15 hr at  $600^\circ\text{C}$  to decompose the nitrates and processed in the same manner as the  $\text{ThO}_2\text{-U}_3\text{O}_8$  mixtures.

The results of sintering these materials at 1500 and  $1750^\circ\text{C}$  are shown in Table II. In general, sintered bulk densities were improved over those previously obtained. Densities obtained using the codigested materials were generally higher than those for the  $\text{U}_3\text{O}_8\text{-ThO}_2$  mixtures sintered at  $1500^\circ\text{C}$ . Samples sintered at  $1750^\circ\text{C}$  were less dense than those sintered at  $1500^\circ\text{C}$ . Such an effect could result either from  $\text{UO}_2$  loss during sintering or oxidation during cooling.

The initial experiments resulted in relatively low densities, and additional studies were made to improve density. Increasing the sintering temperature to  $1830^\circ\text{C}$  for this series of compositions resulted in increased densities. Samples containing less than 60 w/o urania were sintered in air at  $1830^\circ\text{C}$  without any noticeable cracking. At this sintering temperature, the densities varied from  $10.0 \text{ g/cc}$  for the 10-w/o  $\text{UO}_2$  samples, to  $8.8 \text{ g/cc}$  for the samples containing 90 w/o  $\text{UO}_2$ . To aid in stabilization and densification, 0.5 to 1 w/o  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{CaF}_2$  were added to compositions containing up to 25 w/o  $\text{UO}_2$ , and 2.5 w/o  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{CaF}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2$  were added to compositions containing 60 w/o

TABLE II. Effects of Preparation and Sintering on Solid-solution Properties

Preparation and Sintering	ThO <sub>2</sub> , m/o	UO <sub>2</sub> , m/o	Theoretical Density,* g/cc	Sintered Density		Porosity	
				Bulk, g/cc	Theoretical, %	% Open	% Closed
Codigested solid solution** sintered 24 hr at 1750°C	27	73	10.7	8.7	81.2	18.1	0.7
	46	54	10.5	8.9	84.6	15.3	0.1
	66	34	10.3	9.3	90.0	7.1	2.9
Codigested solid solution sin- tered 26 hr at 1500°C	27	73	10.7	9.3	86.8	13.2	0.0
	46	54	10.5	9.3	89.0	10.2	0.3
	66	34	10.3	9.7	94.0	9.0	0.0
ThO <sub>2</sub> -U <sub>3</sub> O <sub>8</sub> mixtures sintered 12 hr at 1500°C	30	70	10.7	9.8	92.3	0.0	7.7
	50	50	10.5	8.7	83.1	5.7	11.2
	70	30	10.3	8.4	81.3	17.2	1.5

\*Calculated from ideal cation lattice corresponding to UO<sub>2.00</sub>.

\*\*Codigestion of soluble nitrates.

To follow the densification behavior in more detail, samples were prepared of a 30m/oThO<sub>2</sub>-70m/oUO<sub>2</sub> mixture and subjected to a draw-trial test procedure. Cylindrical specimens were formed by pressing at 1406 kg/cm<sup>2</sup>, using ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> as the materials along with a binder addition of 3% polyethylene glycol. Specimens were slowly heated to 600°C and held to remove the binder and then heated to 1000°C as the first step for study. Samples for study were drawn from the furnace after 3 hr at this temperature and similar draw trials were made at intervals of 100°C up to 1500°C. The results of this test are shown in Table I. Solid solution began to form at 1000°C and was essentially complete above 1200°C. Shrinkage and density data showed that densification was most rapid in the temperature range of 1200-1300°C. At 1400°C, densification was essentially complete; above this temperature, cracking was evident in the samples.

The draw-trial technique introduces sudden cooling of the sample, which may account for the cracking observed. Further tests were made by using 30m/oThO<sub>2</sub>-70m/oUO<sub>2</sub> and 90m/oThO<sub>2</sub>-10m/oUO<sub>2</sub> samples, prepared as outlined above and sintered at various temperatures up to 1800°C. Samples were held at maximum temperature for 1 hr and slowly cooled to room temperature. The results of linear-shrinkage and bulk-density measurements for these samples are tabulated in Table III and shown graphically in Figs. 5 and 6.

The shrinkage curves for both compositions consisted of essentially two straight lines with an inflection point at approximately 1300°C. The change in rate of shrinkage occurs at about the same temperature at which the solid-solution reaction is completed. Evidently the major shrinkage occurs during solid-solution formation, and, at higher temperatures, shrinkage occurs at a lower rate during consolidation and removal of the pores.



TABLE III. Effect of Temperature on Sintered Properties of ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> Mixtures

Sintering Temperature, °C	Composition*			
	30w/oThO <sub>2</sub> -70w/oUO <sub>2</sub>		90w/oThO <sub>2</sub> -10w/oUO <sub>2</sub>	
	Sintering Shrinkage, %	Sintered Bulk Density, g/cc	Sintering Shrinkage, %	Sintered Bulk Density, g/cc
1100	0.5	4.7	4.4	6.95
1200	4.5	5.9	6.9	7.55
1300	10.7	8.5	9.5	8.15
1400	12.2	9.7	10.0	8.45
1500	12.9	9.8	11.0	8.6
1725	-	-	12.0	8.95
1800	-	-	12.3	9.10

\*UO<sub>2</sub> added as equivalent U<sub>3</sub>O<sub>8</sub> for air sintering.

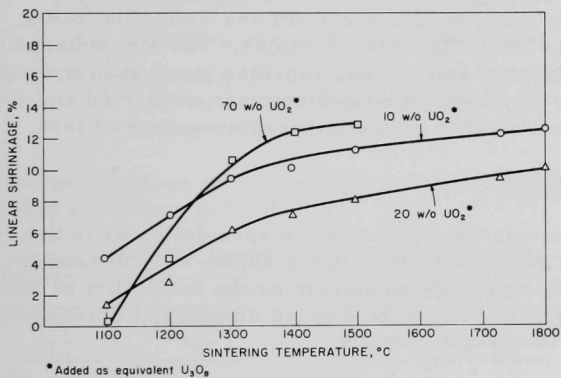
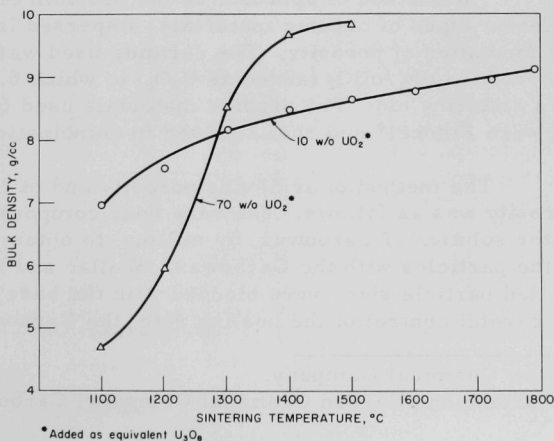


Fig. 5

Effects of Sintering Temperature on Shrinkage of ThO<sub>2</sub>-UO<sub>2</sub> Compositions

Fig. 6  
Effects of Sintering Temperature on Bulk Density of ThO<sub>2</sub>-UO<sub>2</sub> Compositions



The densification curves (Fig. 6) showed the same tendency for an inflection point, although it was almost absent for the 10-m/o  $\text{UO}_2$  composition. The higher  $\text{UO}_2$  composition densified at a considerably faster rate and was essentially constant at  $1500^\circ\text{C}$ .

Compositions in the range of 30 to 70 w/o  $\text{UO}_2$  (added as  $\text{U}_3\text{O}_8$ ) were fabricated and sintered in hydrogen at  $1800^\circ\text{C}$  and in air at the same temperature for comparison of stability. X-ray analysis indicated incomplete solid-solution formation resulting from the hydrogen sintering. Samples were reheated in air at 300, 400, and  $600^\circ\text{C}$ , and chemical analysis was made to determine the oxygen-to-uranium ratio. Hydrogen-sintered samples, reheated in air, disintegrated at  $600^\circ\text{C}$  and after 72 hr at  $400^\circ\text{C}$ , but showed no apparent change after 15 hr at  $300^\circ\text{C}$ . Air-sintered samples were unaffected by the same treatments. Chemical analysis showed the O/U ratios for the air-sintered samples to be in the range of 2.2 to 2.4 before and after reheating. The hydrogen-sintered samples had an O/U ratio of 2.00 after sintering, but when reheated at  $600^\circ\text{C}$ , the O/U ratios were 2.48, 2.37, and 2.22, respectively, for the  $\text{ThO}_2$ -70w/o  $\text{UO}_2$ ,  $\text{ThO}_2$ -50w/o  $\text{UO}_2$ , and  $\text{ThO}_2$ -30w/o  $\text{UO}_2$  solid solutions. The air-sintered solid solutions were much more stable when reheated in air than hydrogen-sintered materials, since they were nonstoichiometric as formed and did not oxidize appreciably on reheating in the temperature range of test.

#### Controlled-porosity Compacts

There has been considerable interest and speculation as to the role of porosity and density of ceramic fuels on their ability to withstand irradiation damage. A study was made to determine the feasibility of fabricating samples containing variable and controlled amounts of closed and open porosity in addition to variable density.

The method of approach to the problem embodied the use of two different types of organic materials, dispersed in the ceramic, to promote the formation of porosity. The ceramic used was a composition of 90w/o  $\text{ThO}_2$ -10w/o  $\text{UO}_2$  (added as  $\text{U}_3\text{O}_8$ ) to which 0.5 w/o  $\text{CaF}_2$  was added as a sintering aid. The organic materials used for the formation of porosity were Ethocel\* and shellac, used in combination with Carbowax.\*\*

The method of achieving porosity and of controlling the closed porosity was as follows: The base body composition was blended with a water solution of Carbowax, by milling, to obtain a thin, uniform coating of the particles with the Carbowax. Shellac and Ethocel grains, of controlled particle size, were blended with the base composition to form voids. By careful control of the heating rate, the Carbowax was removed at a

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\*Dow Chemical Company.

\*\*Carbide and Carbon Chemical Company, Carbowax 4000.

low temperature to provide an open structure in the compact through which the gases evolved from the burnout of shellac and Ethocel could escape, at a somewhat higher temperature, without structural damage to the compacted sample. During the sintering process, the sample densified around the individual voids left by these grains and thus produced the closed porosity desired.

### Series I

The initial series of samples prepared was based on the fuel composition 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub>, with 0.5 w/o CaF<sub>2</sub> added, and prepared by using different combinations of the following variables:

1. Forming and structure-opening binder: Carbowax 3 or 6 w/o.
2. Burnout grain for void formation: Ethocel or shellac; 0, 10, or 20 w/o of -60 +100 mesh grain or -100 +170 mesh grain.
3. Forming pressure (cold compaction): 700 and 1400 kg/cm<sup>2</sup>.
4. Sintering exposure: samples placed in open or closed containers.
5. Sintering treatments: (a) 4 hr at 1680°C, (b) 2 hr at 1800°C, or (c) 9 hr at 1750°C with a 19-hr soak in the range of 1400-1450°C during the heating cycle.

The compositions of the samples and the variables imposed for the initial series are shown in Table IV.

TABLE IV. Compositions of Variable-porosity Samples Prior to Sintering

90w/oThO <sub>2</sub> -10w/oUO <sub>2</sub> with 0.5 w/o CaF <sub>2</sub> Added				
Batch No.*	Carbowax, w/o	Grain,** v/o	Grain Size,** mesh	Forming Pressure, 10 <sup>-3</sup> kg/cm <sup>2</sup>
1-LC	3	-	-	0.7
1-HC	3	-	-	1.4
2-LC	6	-	-	0.7
2-HC	6	-	-	1.4
8-E	3	10	-100 +170	1.4
10-E	3	20	-100 +170	1.4
12-E	6	10	-60 +100	1.4
13-E	6	20	-60 +100	0.7
14-E	6	20	-60 +100	1.4
15-E	6	10	-100 +170	0.7
16-E	6	10	-100 +170	1.4
17-E	6	20	-100 +170	0.7
18-E	6	20	-100 +170	1.4
7-S	3	10	-100 +170	0.7
8-S	3	10	-100 +170	1.4
9-S	3	20	-100 +170	0.7
13-S	6	20	-60 +100	0.7
16-S	6	10	-100 +170	1.4

\*C = Control pellets.

E = Ethocel grain used in pellets.

S = Shellac grain used in pellets.

\*\*Refers to combustible Ethocel or shellac grains.

Sintering of this series at 1680°C resulted in low-density samples. The highest bulk density achieved was 79.3% theoretical for those samples that contained no pore-forming additives. Because of the small amount of densification obtained by this treatment, the amount of closed porosity formed was small. The closed porosities obtained were in the range of 1 to 5 v/o; the total porosities varied from 21 to 40 v/o.

Sintering at 1800°C increased the density of the control samples to 87% theoretical. As a result of the increased densification, the total porosities decreased to a range of 13 to 34 v/o, and the closed porosities increased to a range of 1 to 11 v/o.

The sintering treatment at 1750°C was designed to allow more time for sintering to occur in the lower temperature range. As a result, the control samples achieved a density of 90.7% theoretical. The total porosity was in the range of 9 to 30 v/o, and the closed-porosity variation was from 7 to 18 v/o.

The range of values desired for porosities in these samples was from 4 to 20 v/o closed porosity, and with an open porosity as low as possible, preferably 1 v/o or less. Following the 1750°C sintering treatment, most of the samples were found to have 2 to 4 v/o open porosity, although some of the control samples exhibited as low as 0.5 v/o open porosity. The most suitable specimen in the low void range was a control sample that had 7.3 v/o closed porosity and 2.0 v/o open porosity. The most promising compositions for producing high-porosity samples were: (1) samples containing 10 v/o addition of -100 +170 mesh Ethocel, which had 16.4 v/o closed porosity and 2.4 v/o open porosity; and (2) samples containing 10 v/o addition of -60 +100 mesh shellac, which resulted in 17.8 v/o closed porosity and 4.1 v/o open porosity.

The other variables introduced into this system showed the following general effects:

1. Variation in the amount of Carbowax had little effect on the sintered properties of the specimens. An exception was in the case of the samples containing shellac; those containing 6 w/o Carbowax cracked during sintering, but those containing 3 w/o Carbowax did not.
2. Samples containing 20 v/o of burnout grain resulted in a higher percentage of open porosity than did those having the 10 v/o addition.
3. The pressure variations used gave results indicating an even higher pressing pressure to be desirable. The resistance to cracking and strength of the pellets was considerably improved by increased pressure during forming.



4. The use of closed containers for the samples during sintering resulted in an undesirable surface-densification effect.

Different types of pores were formed by the two additives as a result of the effect of pressure on the grains. Ethocel grains tended to flatten in a plane perpendicular to the direction of pressure application and did not recover after the release of pressure. The shellac grains deformed in a similar manner but, either to a lesser degree, or they deformed elastically and returned essentially to their original shape after the release of pressure.

Specimens prepared in this first series were in the acceptable range for closed porosity but were high in open porosity and, in addition, showed considerable cracking during the burnout period.

### Series II

A second series of specimens was prepared in which changes designed to increase the sinterability of the base composition were made as follows:

1. The  $\text{CaF}_2$  content was increased from 0.5 to 20 w/o and added as minus 325-mesh particles for better dispersion and increased sintering action.
2. Particles greater than 200-mesh size were eliminated from the  $\text{U}_3\text{O}_8$  and  $\text{ThO}_2$  before milling.
3. Specimens were fabricated by preforming at  $350 \text{ kg/cm}^2$  in a steel die and then by isostatic pressing at  $3850 \text{ kg/cm}^2$ .

Samples fabricated in this manner were sintered for 10 hr at  $1750^\circ\text{C}$ , and the average bulk density achieved was 92% theoretical. Cracking was evident in the samples containing Ethocel as the pore-forming additive. The cracks formed during the period of removal of the additive and did not heal during sintering. Determinations were made to establish when cracking occurred during the burnout cycle and the role of grain size of the additive. Shellac grains in the size ranges of -150 +170 mesh, -170 +200 mesh, -200 +325 mesh, and -325 mesh were used. Regardless of how carefully the burnout cycle was controlled, specimens containing -140 +170 mesh and -170 +200 mesh grains developed cracks when a burnout of greater than 83% of the shellac was reached. Samples containing finer grain-size shellac were capable of higher burnout without cracking, and some with minus 325-mesh additive achieved complete removal of the shellac without cracking.

The addition of 2 w/o  $\text{CaF}_2$  increased the sintered density of the base composition to some extent, but there were surface indications that this amount might be excessive.

### Series III

For the third series of compositions, the base composition was set at 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> (as U<sub>3</sub>O<sub>8</sub>) with 1 w/o CaF<sub>2</sub> added and 3 w/o Carbowax as the pressing binder and burnout material to open the structure for shellac removal. Greatly increased milling times of 24, 48, and 72 hr were used to reduce the particle size and improve the distribution of particles, thus increasing the sinterability of the compacts. Samples of this material, when fabricated by isostatic pressing at 3850 kg/cm<sup>2</sup> and sintered for 10 hr at 1750°C, had densities in the range of 95 to 96% theoretical.

Burnout tests were made of this composition containing 10 v/o additions of -200 +325 mesh, -200 +400 mesh, -325 mesh, and -400 mesh shellac grains and -200 +325 mesh, -200 mesh, and -400 mesh Ethocel grains. For these samples, a burnout of 90% of the additive was achieved in a 24-hr cycle with no evidence of cracking in the compacted shapes.

Samples containing Ethocel were not satisfactory when sintered for 10 hr at 1750°C, but those containing shellac were suitable and yielded porosity values as shown in Table V.

TABLE V. Porosities Achieved with Shellac Additive to Base Composition\*

Shellac Grains	Added, v/o	Closed Porosity, v/o	Open Porosity, v/o
-	0	4.1	0.0
-200 +325	10	9.0	0.5
-200 +400	10	9.5	0.8
-325	10	8.9	2.0
-400	10	8.8	1.1

\*90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> (as U<sub>3</sub>O<sub>8</sub>) + 1 w/o CaF<sub>2</sub>.

The most satisfactory samples produced were those containing -200 +400 mesh particles of shellac as the additive for void formation. With the information resulting from the study of this series, samples containing enriched material were prepared for irradiation study. Details concerning these samples follow in this report under the heading Irradiation Specimens.

### Compatibility

A series of samples was made to determine the possibility of reactions between the following systems: 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> and Zircaloy-2, 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> and stainless steel, 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> and graphite, and graphite with Zircaloy-2.

The thoria-urania samples for these tests were a composition of 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> prepared by cold-pressing of mixed oxides and sintering at 1750°C. Sample pellets were loaded into tubes of Zircaloy-2, stainless steel, or graphite. In one case, the annulus between the stainless-steel tube and the pellet was filled with lead. One sample was also made in which pellets of 90w/oThO<sub>2</sub>-10w/oUO<sub>2</sub> and pellets of Zircaloy-2 were in contact. Samples were also made of Zircaloy-2 and stainless-steel tubes filled with lead. After preparation, all samples were encased in Vycor tubes and sealed. One set of samples was heated to 600°C, and a second set to 800°C for a period of 60 days, following which they were examined metallographically to determine the extent of reactions.

Representative photomicrographs are shown in Figs. 7 to 10. No reactions were observed in these systems after the heat treatment at 600°C for 60 days. When the samples were heated to 800°C for 60 days, a reaction zone developed between the lead and the Zircaloy-2. No other reactions were observed by metallographic techniques following the heat treatment at 800°C.

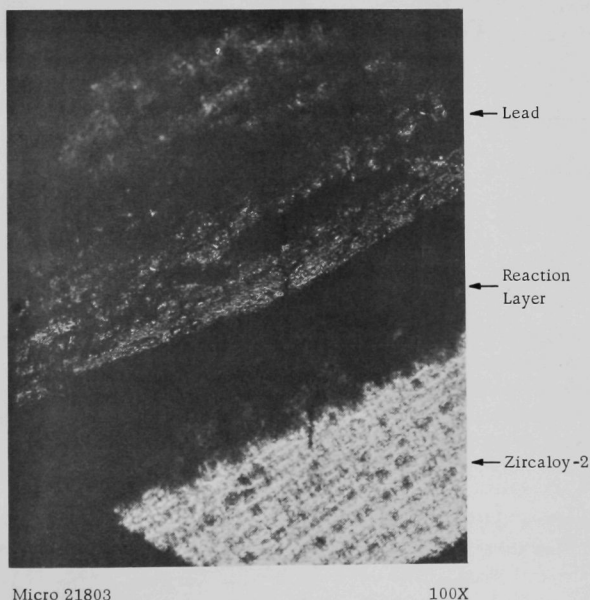


Fig. 7. Lead and Zircaloy-2 Compatibility Samples (heated 60 days at 800°C)



Fig. 8. ThO<sub>2</sub>-UO<sub>2</sub> Pellets in Stainless-steel Capsule with a Lead-filled Annulus (heated 60 days at 800°C)

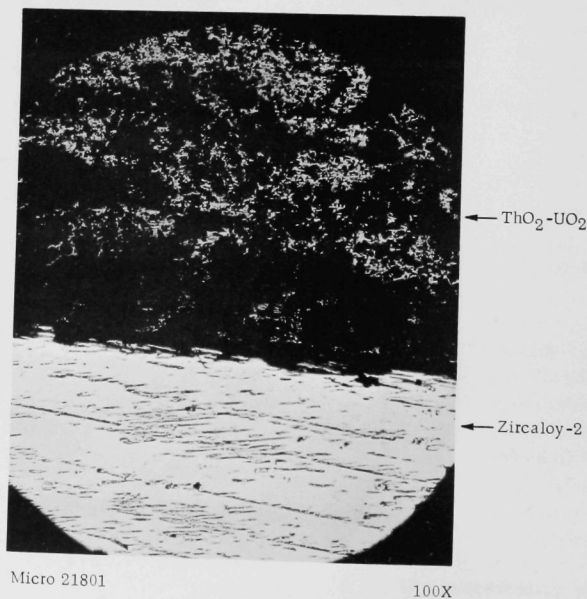


Fig. 9. ThO<sub>2</sub>-UO<sub>2</sub> Pellet in Zircaloy-2 Cylinder (heated 60 days at 800°C)

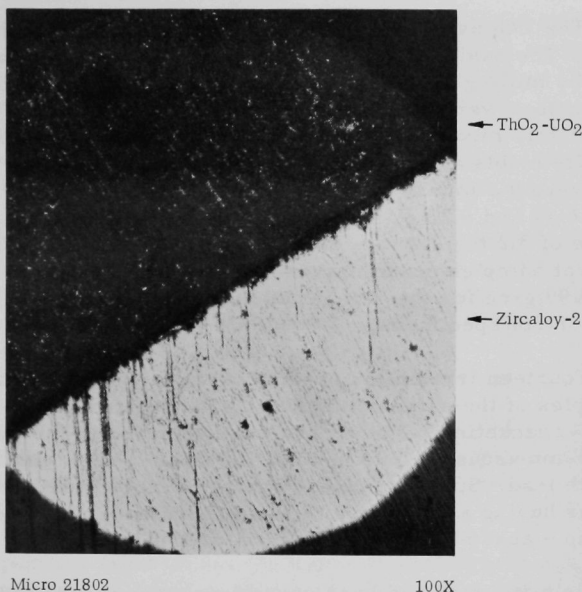


Fig. 10.  $\text{ThO}_2\text{-UO}_2$  Pellet in Contact  
with Zircaloy-2 Pellet  
(heated 60 days at  $800^\circ\text{C}$ )

## Irradiation Specimens

### Metal-Fiber-reinforced Thoria-Urania

Interest in the irradiation behavior of thoria-uranium, reinforced by metal fibers, developed as a result of work conducted at Armour Research Foundation and reported by Baskin *et al.*<sup>12</sup> Of special interest in these reports was the improvement in high-temperature thermal conductivity of thoria when metal fibers were added and the improvement in resistance to thermal spalling.

To establish parameters for possible further studies, a range of compositions was selected for evaluation. The base oxide compositions used were 90w/o $\text{ThO}_2$ -10w/o $\text{UO}_2$ , 70w/o $\text{ThO}_2$ -30w/o $\text{UO}_2$ , and 50w/o $\text{ThO}_2$ -50w/o $\text{UO}_2$ . The 10 w/o  $\text{UO}_2$  compositions were 93.2% enriched in  $\text{U}^{235}$ ; the 30 w/o and 50 w/o  $\text{UO}_2$  compositions were 19.2% enriched. Samples were fabricated of the base compositions without additions, and of the base compositions in which additions of fibrous molybdenum or niobium made up approximately 10 w/o of the combined oxide-fiber weight. The fibers were all nominally 3.2 mm long, and the diameters were 0.13 and 0.25 mm for the molybdenum and niobium, respectively.

The  $\text{UO}_2$  used was produced by hydrogen reduction of  $\text{U}_3\text{O}_8$  at  $800^\circ\text{C}$  for 4 hr. The oxides, together with an addition of 0.5 w/o  $\text{CaF}_2$ , were blended by milling for 24 hr. Before fabrication, the oxides and metal-fiber additions were weighed in increments sufficient to form one sample and intimately mixed by hand. Samples were fabricated by hot-pressing in graphite molds at  $1500^\circ\text{C}$  under  $175 \text{ kg/cm}^2$  pressure. The specimens formed were 9.5 mm in diameter, approximately 9.5 mm long, and weighed between 6.17 and 8.28 g. The fabricated porosities of the samples were in the range of 3.2 to 12.2 v/o for the fibered samples, and 3.8 to 17.4 v/o for the control samples containing no fibers. Bulk density values varied from 9.30 to 9.99 g/cc for the reinforced samples, and from 8.53 to 10.05 g/cc for the control specimens.

Fourteen irradiation specimens were prepared, each containing two samples of the same composition and jacketed in 0.5-mm-wall Zircaloy-2 jacketing. The pellets were centered in the jackets by use of three 1.6-mm-square, longitudinal, Zircaloy-2 ribs, and the annulus was filled with lead. Six other specimens were fabricated in the same manner except for having a 0.025-mm, helium-filled annulus. End caps on the clad sample assemblies were Heliarc-welded.

Both jacketed and bare specimens were irradiated singly in aluminum NaK capsules, the space above the NaK being evacuated to  $0.2 \mu \text{ Hg}$ . Stainless-steel wool was used in the annulus to center the samples in the capsule and to prevent damage from mechanical shock. Each capsule contained an aluminum-cobalt flux monitor, which was used in determining the burnup and heat output of the specimen.

Irradiation studies were made by the ANL Engineering Irradiation Group of the Metallurgy Division, and details have been reported by Neimark *et al.*<sup>13,14</sup> Their conclusions are summarized briefly here for purposes of continuity.

Irradiations were carried out in the ETR and were designed to give a range of burnups to a maximum of about 30,000 MWD/T and maximum central fuel temperature of  $3200^\circ\text{C}$ .

One lead-bonded, molybdenum-fibered specimen that received a burnup of about 31,000 MWD/T showed cladding rupture and a longitudinal crack. The jacketing on five of the six helium-bonded samples had melted through or showed signs of melting.

Bare specimens containing no fibers ruptured into many small fragments. Fibered specimens, irradiated unclad, broke into only two or three pieces and in some cases did not break. Volume increases for clad specimens ranged from zero to 1.0% for lead-bonded samples and from 0.4% to 1.8% for helium-bonded specimens.



Improvement in thermal conductivity by the addition of fibers was shown by the increased resistance to thermal stress and by the differences in central void formation. Samples that did not contain fibers were severely cracked during irradiation. When metal fibers were used, the central void did not form or was diminished in size in comparison to unfibered samples with comparable heat ratings. In all cases, niobium fibers showed reactions with the environment and were not satisfactory.

The addition of molybdenum fibers to the base  $\text{ThO}_2\text{-UO}_2$  composition permitted higher heat ratings before comparable thermal effects occurred. The fibers tended to reduce central void formation, retard recrystallization, and maintain the integrity of the fuel pellets.

### Variable-porosity Fuel Pellets

For irradiation studies, samples having a sintered composition of  $89\text{w/o ThO}_2\text{-}10\text{w/o UO}_2\text{-}1\text{w/o CaF}_2$  were fabricated with controlled amounts of open and closed porosity. The  $\text{UO}_2$  addition was made by using  $\text{U}_3\text{O}_8$  which was approximately 93% enriched  $\text{U}^{235}$ .

In preparation for fabrication, the base composition was milled for 48 hr with an addition of 3 w/o of Carbowax, dried, and passed through a 100-mesh sieve. To form voids in the structure, shellac grain additions in the range of 0 to 21 v/o were blended with the base composition. The grain size of the shellac was -200 +400 mesh. Samples were preformed by pressing in a steel die at  $350 \text{ kg/cm}^2$  to a size of approximately 0.64 cm diam by 1.3 cm long. Preformed samples were then isostatically compacted under a pressure of  $3850 \text{ kg/cm}^2$ . Shellac grains were burned out at low temperature before final sintering at  $1750^\circ\text{C}$  for periods from 16 to 72 hr.

To evaluate the fabrication procedure, microscopic examination was made on transverse sections of two representative pellets which had the following characteristics:

Description	Theoretical Density, %	Open Porosity, v/o	Closed Porosity, v/o
Base Composition	95.1	0.1	4.8
10 v/o Shellac Addition	89.6	0.8	9.6

The base composition had uniformly distributed voids of 1 to 8 microns diameter and all appeared to be closed. No capillary pore networks extended to any depth in the pellet. The open porosity shown by this sample can be attributed to pores occurring at or near the surface.

The base composition with 10-v/o-shellac addition showed two distinct sizes of pores uniformly dispersed throughout the sample. Part of the pores were in the 1- to 8-micron size range found previously; the majority ranged from 18 to 42 microns in diameter. These larger pores resulted from the burnout of the shellac grains. Some of the larger pores were found to connect but not to open to the surface. The increase in open porosity was due to an increase in the size and number of surface pores.

Representative values for porosity and density of the irradiation samples are shown in Table VI. From the information gathered by microscopic study, it is reasonable to expect that an open-pore capillary structure does not begin to permeate the sample to an appreciable depth until about 2 v/o open porosity exists.

TABLE VI. Characteristics of Irradiation Samples

Theoretical Density, %	Open Pores, v/o	Closed Pores, v/o
<u>Representative Values</u>		
93.0	0.2	6.8
91.3	0.3	8.4
89.1	0.6	10.3
87.7	0.8	11.5
85.2	1.2	13.6
82.8	2.1	15.1
81.3	8.3	10.4
79.8	12.5	7.7
	Open Porosity, v/o	Theoretical Density, %
<u>Reliability of Measurements</u>		
Pellets with open porosity 0.50 v/o	±0.03	±0.05
Pellets with open porosity 0.50-1.50 v/o	±0.06	±0.08
Pellets with open porosity 1.50 v/o	±0.10	±0.12
All samples	±0.20	±0.50

These samples were irradiated in two sets. Postirradiation examinations have been completed on one set, and a preliminary report was made by Neimark.<sup>15</sup>

Irradiation was carried out in NaK capsules with one unclad fuel pellet per capsule. Burnups achieved were in the range of 17,000 to 22,900 MWD/T at initial integral  $kd\theta$  ratings between 31 and 50 W/cm.

Cracking of samples made evaluation of irradiation effects difficult. To help alleviate this problem, a second set of samples has been irradiated containing four pellets per capsule. Irradiation conditions were approximately 10,000 MWD/T burnup and an integral  $kd\theta$  of 20 W/cm. Postirradiation examination of these samples is in progress.

During this program work, a considerable interest developed in the use of ceramic fuels in thermal reactors and specifically for the BORAX-IV reactor. As a result, a wide variety of irradiation specimens was prepared to evaluate fuel characteristics, bonding, cladding, and safety of the thorium-uranium fuels.

The samples prepared were similar in nature, and the major variables in the testing program were irradiation treatment, jacketing, and bond. Samples prepared for testing were either  $\text{ThO}_2\text{-}2.5\text{w/oUO}_2$  or  $\text{ThO}_2\text{-}10\text{w/oUO}_2$  and were prepared by pressing  $\text{ThO}_2\text{-U}_3\text{O}_8$  mixtures. These samples were sintered in an atmosphere of air in the temperature range of 1750-1800°C.

The results of these irradiation tests have been reported.<sup>16</sup>

## SUMMARY

Thorium-uranium compositions may be fabricated by any of the common ceramic methods such as dry-pressing, hot-pressing, slip-casting, and extrusion. Two general procedures have been established for the production by dry-pressing of small quantities of material and large quantities of shapes. For the production of large quantities of shapes, it was necessary to provide a free-flowing powder for automatic pressing equipment.

Mixtures of  $\text{ThO}_2\text{-U}_3\text{O}_8$  sintered to high density when heated in air to temperatures near 1700°C. Samples heated in the same manner in hydrogen did not show a complete solid-solution development as did the air-sintered materials. Draw-trial tests during sintering showed the major dimensional changes during heating to occur in the temperature range of solid-solution development.

It was demonstrated that samples of controlled open and closed porosity could be prepared by the manipulation of Carbowax and shellac in the base composition. By means of the technique developed, irradiation specimens were prepared having open porosity in the range of 0.2 to 12.5 v/o and closed porosity in the range of 6.8 to 15.1 v/o.

Irradiation specimens containing metal fibers were prepared by hot-pressing. The addition of fibers increased the resistance to thermal stress under irradiation, with a resulting decrease in specimen cracking and elimination or decrease of the central void.

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